A Reactor-design Equation Based on a Proposed Distributed Boundary-layer Thickness

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An empirical equation is developed which seems applicable to the general problem of fixed-bed catalytic-reactor design and relates the reaction rate (in a differential reactor) or conversion (through an integral reactor) to the surface reaction rate, the flow rate through the bed, and the physical properties of the system. The development is based on the assumption that there exists a film of stagnant fluid surrounding each catalyst particle, through which mass is transferred only by molecular motion, and that the thickness of this film varies throughout the bed from zero to some upper limit in a manner which is described by a distribution function. The equation involves two empirical constants: the multiplying constant and the exponent in the usual j_d-factor–Reynolds-number relationship.

The application of this equation is illustrated. It appears to provide a basis for evaluation of the contribution of diffusional steps in the over-all mechanism and to provide a means for predicting an expected conversion rate at any flow rate through the bed, provided only that the surface (chemical) reaction rate is known at the operating temperature. It also appears possible to calculate values of the surface-reaction-rate constant and the temperature coefficient from data taken from a reactor operating in the diffusion-controlled range.

The rational design of a fixed-bed catalytic reactor requires an understanding of the mass and heat transfer phenomena occurring, as well as of the chemical reaction kinetics. Of these, the detailed description of mass transfer rates between fluid phase and particle surface has received least attention to date.

There have been many studies of the gross nature of this problem. Over-all mass transfer coefficients, j factors, transfer-unit concepts, and other macroscopic analyses are common in chemical engineering literature. Such analyses gloss over the detailed point-to-point conditions in a packed bed and ascribe over-all behavior to averaged characteristics and properties.

It seems obvious that the catalyst surface area in a packed-bed reactor is not uniformly available. There must exist a film of fluid over the external particle surfaces which is essentially stagnant and through which reactant and product are transported by molecular motion only. It is furthermore obvious that the thickness of this film, for any flow rate through the bed, must vary from point to point over a given catalyst particle. This variation throughout the bed is between zero and some upper limit, which should be determined by the particle diameter and packing geometry.

At any specific location on the catalyst surface, the rate of diffusion of reactant to the surface will be determined by the film thickness at that point and by the concentration of reactant in the bulk of the fluid and at the surface. Furthermore, at this point, as at all points, the diffusion rate equals the rate of chemical reaction on the surface. The latter is determined by the concentration of reactant at the surface. The net rate of production of product by chemical reaction at the surface will vary with film thickness, as shown in Figure 1. Since the relationship between *rate* and *film thickness* is of a reciprocal nature, the following development will be expressed in terms of $1/\delta$.

For any real situation, it is obvious that the rate must continue to increase as $1/\delta \to \infty$ but in such a manner that $dr/d(1/\delta) \to 0$ as $1/\delta \to \infty$. Furthermore, the maximum rate, the value where $dr/d(1/\delta) = 0$, must be finite. Thus one may define a value of film thickness such that for $1/\delta \geq 1/\delta_c$ the measured rate is different from the maximum, or ultimate, value only by the probable error of measurement or less. This is shown schematically in Figure 1. For any value of $1/\delta > 1/\delta_c$ the surface reaction rate does not change appreciably. This is the *reaction-controlled* region. For $1/\delta < 1/\delta_c$ the surface concentration of reactant and, hence, the surface reaction rate is affected measurably by changes in $1/\delta$ and therefore by changes in flow rate. This is the *diffusion-controlled* region. Certainly this is oversimplified; however, it will serve to illustrate the physical meaning and significance of the critical *film thickness* δ_c.

It is assumed, then, that the bed surface areas can be divided into two kinds. The first are those surfaces over which $1/\delta > 1/\delta_c$, where the surface concentration of reactant will be essentially constant at a fraction of the free stream concentration approaching unity. The second types of surfaces are those over which $1/\delta < 1/\delta_c$, where the surface reaction rate will be fast by comparison to the rate of supply of reactant to the surface and the surface concentration of reactant will be low.

For convenience, a dimensionless film thickness is defined as

$$x = \frac{\delta}{\delta_{max}} \tag{1}$$

where δ_{max} is the maximum possible film thickness in the particular bed under discussion. For the present, no attempt will be made to identify this in terms of bed geometry. However, it will be noted that $0 < x < 1$ at all points.

It will be interesting to seek a function of x to represent the distribution of x throughout the bed. The fraction of the bed area over which the dimensionless film thickness (as represented by x) is between two arbitrary values, say x_1 and x_2, may be represented by $(a)_{x_1/x_2}$.

Then the required function must be such that

$$(a)_{x_1/x_2} = \int_{x_1}^{x_2} f(x)\, dx \tag{2}$$

Some of the properties of this function are obvious. First, as x_1 approaches zero and x_2 approaches unity, the function must yield a value of unity in Equation (2). Furthermore, the function must pass through a maximum in the interval $0 \leq x \leq 1$; the value of x at this maximum will be designated by x_m. The function must provide parameters which can be related to the performance of a packed-bed reactor. Thus, for example, as the mass rate of flow through the bed increases, all other variables remaining constant, the form of the $f(x) - x$ relationship must become sharply peaked about a value of $x_m \to 0$. As the mass rate of flow decreases, the relationship must become sharply peaked about a value of $x_m \to 1$. Between these two extremes, a single distribution must be available for all permissible sets of values of parameters such as the Reynolds number (based on particle diameter and flow rate through the empty tower), bed diameter, and possibly particle shape factors.

A function which seems to provide most of these characteristics is the beta distribution of beta density, a well-known distribution function in the field of statistics, of the following form:

$$f(x) = \frac{(\alpha + \beta + 1)!}{\alpha!\beta!} x^{\alpha}(1 - x)^{\beta} \tag{3}$$

It is possible to show (5) that

$$\int_0^1 x^{\alpha}(1 - x)^{\beta}\, dx = \frac{\alpha!\beta!}{(\alpha + \beta + 1)!} \tag{4}$$

and hence that

$$\int_0^1 f(x)\, dx = 1$$

Values of the incomplete beta function, defined as

$$\int_0^x \frac{(\alpha + \beta + 1)!}{\alpha!\beta!} x^{\alpha}(1 - x)^{\beta}\, dx \equiv B_x(\alpha, \beta) \tag{5}$$

are tabulated for a wide range of the indicated parameters by Pearson (*8*). It will be noted that

$$B_x(\alpha, \beta) = 0 \text{ for } x \leq 0$$
$$0 < B_x(\alpha, \beta) < 1 \text{ for } 0 < x < 1 \quad (6)$$
$$B_x(\alpha, \beta) = 1 \text{ for } x \geq 1$$

The beta function represents a two-parameter family of distributions, yielding various forms for particular values of α and β. Figure 2 indicates the shape of this function for several sets of values of these parameters. Although there is no reason to expect the beta distribution function to be unique for the purpose of this work, many other functions have been tried without success, none having been found which yield the satisfactory results shown in the following development.

In a fixed-bed catalytic reactor a balance about a differential element taken perpendicular to the axis yields

$$-F\,dy = \left[\int_0^{a_c} r\,da\right] dV + \left[\int_{a_c}^{a} r_d\,da\right] dV \quad (7)$$

Noting then that the surface reaction rate is assumed essentially constant in the range $0 < \delta < \delta_c$ or for $0 < a < a_c$ (see Figure 1) and introducing the distribution function defined by Equation (3) one finds that Equation (7) becomes

$$-\frac{F\,dy}{dV} = r \cdot a \cdot \int_0^{x_c} f(x)\,dx + a \int_{x_c}^{1} r_d f(x)\,dx \quad (8)$$

Both of the integrals on the right-hand side of this equation are multiplied by a since the distribution function as previously defined represents a *fraction* of the total bed area and not the area itself. $dV = A\,dl$ and, approximately,

$$r_d = \frac{D}{\delta}(C_0 - C_i) \quad (9)$$

On the basis of the foregoing information, together with the previous assumption that C_i is negligible by comparison to C_0 for the areas over which $1/\delta_c > 1/\delta > 1/\delta_{max}$ plus Equations (5) and (9), Equation (8) can be transformed to the following:

$$-\frac{F\,dy}{aA\,dl} = rB_{x_c}(\alpha, \beta) + \frac{DC_0}{\delta_{max}} \int_{x_c}^{1} \frac{f(x)}{x}\,dx \quad (10)$$

In Equations (9) and (10) concentrations C are used rather than mole fractions y for dimensional reasons. Furthermore, $C/\rho = y$, where ρ is the average molal density. It can be shown that

$$\int_{x_c}^{1} \frac{f(x)}{x}\,dx = \frac{\alpha + \beta + 1}{\alpha} \cdot [1 - B_{x_c}(\alpha - 1, \beta)] \quad (11)$$

and thus

$$-\frac{F\,dy}{aA\,dl} = rB_{x_c}(\alpha, \beta) + \frac{\rho D y_0(\alpha + \beta + 1)}{\alpha\,\delta_{max}} \cdot [1 - B_{x_c}(\alpha - 1, \beta)] \quad (12)$$

This then is the final result. It should apply to a differential volume element of a fixed-bed catalytic reactor provided only that the true distribution of x over the area in that element can be represented by the beta distribution function and that the assumptions involved in the designation of $1/\delta_c$ are valid. The former involves only a curve fitting problem and the relating of the two arbitrary parameters to physically determinable variables. The assumption of a nonzero value of $1/\delta_c$ involves questions concerning the sensitivity with which the rate (or composition in the exit gases) can be measured for a specific problem to yield physically meaningful results and the shape of the relationship shown in Figure 1. The latter, in turn, depends upon the ratio of molecular diffusivity to surface reaction rate constant.

Two limiting cases will now be considered, namely, the form of Equation (12) resulting from setting x_c equal to the two permissible extreme values, 0 and 1. With $x_c = 0$, equivalent to $1/\delta = \infty$, the problem becomes one of pure diffusion involving a reaction at the surface which is infinitely fast (with zero energy of activation). Such a situation would be approximated by a gas-liquid adsorption process in a packed bed wherein the gas film controls. For this case, Equation (12) becomes

$$-\frac{F\,dy}{aA\,dl} = \frac{\alpha + \beta + 1}{\alpha} \frac{\rho D y_0}{\delta_{max}} \quad (13)$$

For the other extreme, that is, with $x_c = 1$, it is apparent that $1/\delta_c = 1/\delta_{max}$ (indicating that the minimum permissible value of $1/\delta$ used in Figure 1 is properly nonzero). This case corresponds to a process which is reaction controlled throughout over all ranges of flow; that is, molecular diffusion is very fast by comparison to the chemical reaction at the surface, and Equation (12) should and does reduce to

$$-\frac{F\,dy}{aA\,dl} = r \quad (14)$$

The latter is the familiar result presented, for example, by Hougen and Watson (*2*).

Equation (13), being a diffusion equation, may be used to obtain some information concerning the relationship between α and β and the variables of importance in diffusion processes. If both parameters, flow rate, and density are assumed constant, this equation may be integrated to yield

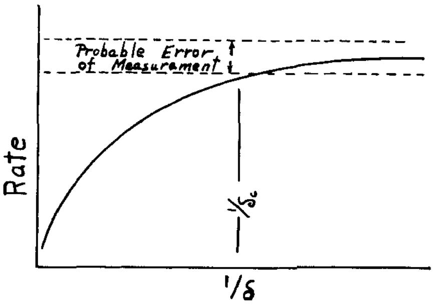

Fig. 1. Schematic rate curve.

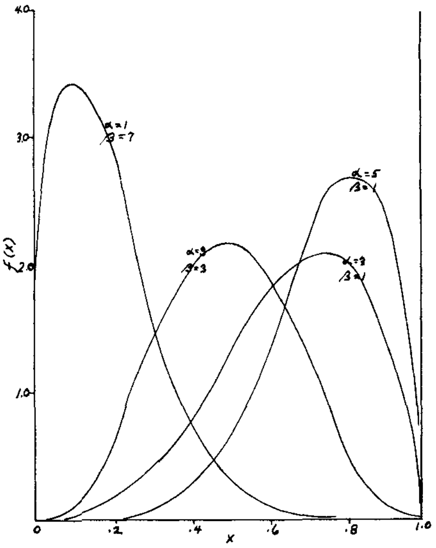

Fig. 2. The beta function.

$$\ln \frac{y_{0_1}}{y_{0_2}} = \frac{\rho D a A}{\delta_{max}} \cdot \frac{\alpha + \beta + 1}{\alpha} \cdot \frac{L}{F} \quad (15)$$

This result is exactly analogous to the integrated equation for the design of gas-liquid packed-bed absorbers for the case where the gas film controls, provided only that

$$\frac{\rho D}{\delta_{max}} \cdot \frac{\alpha + \beta + 1}{\alpha} = k_g \quad (16)$$

From gas-absorption theory, the mass transfer coefficient is defined as

$$k_g = \frac{DP}{RTB' y_{Bm}} \quad (17)$$

In this equation, B' (the symbol used in gas-absorption references to represent the film, or boundary-layer, thickness) is identical with δ as defined in this paper. Also, $P/RT = \rho$ from the ideal gas law. Thus Equation (16) becomes

$$\frac{\alpha + \beta + 1}{\alpha} = \frac{\delta_{max}}{\delta y_{Bm}} \quad (18)$$

Empirically, k_g is related to the physical properties of the system and to flow rate through the usual j-factor relationship thus:

$$k_g = a' \frac{\mu}{d_p M_m} N_{Sc}^{-2/3} N_{Re}^{1+b} \quad (19)$$

where the constants a' and b are determined from experiment. There is little question about the value of b since the experimental evaluation of this yields -0.51 with reasonable consistency. There is considerable question, however, about the value of a'. [See, for example, the summary of Ergun (*1*).] Some information can be obtained from the following relationship resulting from the combination of Equations (17) and (19):

$$\frac{\delta_{max}}{\delta y_{Bm}} = \frac{a' N_{Sc}^{\frac{1}{3}} N_{Re}^{\frac{1}{2}}}{(d_p/\delta_{max})} \tag{20}$$

The left-hand side of this equation is obviously greater than unity, and, hence, the value of a' on the right must be large enough to make the right-hand side also greater than unity; it must also vary with N_{Re} and y_{Bm}. Thus, the value of a' must depend upon the physical and operational characteristics of the system. This seems wholly reasonable. For the present, a' will be considered an unknown empirically determined constant, and Equation (18) may be combined with Equation (20) to yield

$$\frac{\alpha + \beta + 1}{\alpha} = \frac{a' N_{Sc}^{\frac{1}{3}} N_{Re}^{\frac{1}{2}}}{(d_p/\delta_{max})} \tag{21}$$

It is now necessary to identify α and β with the variables shown in Equation (21). This must necessarily be quite arbitrary and involve assumptions which are wholly *ad hoc.* It is assumed first that α is small compared to $\beta + 1$. Thus, $\alpha < \beta + 1$, and Equation (21) may be considered to be composed of two parts:

$$\alpha = \frac{d_p}{a' \delta_{max} N_{Sc}^{\frac{1}{3}}} = \frac{(\delta/\delta_{max}) y_{Bm}}{N_{Sc}^{\frac{2}{3}} N_{Re}^{\frac{1}{2}}} \tag{22}$$

and

$$\beta + 1 = N_{Re}^{\frac{1}{2}}$$

These definitions are consistent with the characteristics previously required for α and β. The acceptability of these assumptions, or, better, these assignments, can be determined only by the success of the resulting equations. It is evident, however, that the accuracy of the previous statements will be best for large Reynolds numbers, large values of the Schmidt number, or both.

A further simplification of Equation (12) results from a consideration of the possible range of values of $B_{x_c}(\alpha - 1, \beta)$ in Equation (21). From Pearson's tables, it is evident that for $x_c > 0.05$ and $\alpha \leq 0.3$

$$B_{x_c}(\alpha - 1, \beta) \rightarrow 1$$

Examination of the variation of $B_{x_c}(\alpha - 1, \beta)$ with α indicates that as α decreases, the incomplete beta function rapidly approaches unity. For the problem considered in this paper, α is expected to be small. Thus, for such systems one may assume that

$$[1 - B_{x_c}(\alpha - 1, \beta)] \rightarrow 0$$

Equation 12 then becomes:

$$-\frac{F\,dy}{aA\,dl} = rB_{x_c}(\alpha, \beta) \tag{23}$$

This result then is based on the implicit assumption that the fraction of the bed surface areas over which the surface reaction rate is controlling produces essentially all of the product and that the production rate from the remaining surface areas is negligible by comparison.

With the assumption that α is small, the beta function may be integrated and Equation (23) becomes

$$-\frac{F\,dy}{aA\,dl} = r[1 - (1 - x_c)^{\beta+1}] \tag{24}$$

or if Equation (22) is introduced,

$$-\frac{F\,dy}{aA\,dl} = r[1 - (1 - x_c)^{\sqrt{N_{Re}}}] \tag{25}$$

This may be written, for convenience, as

$$-\frac{N_{Re}\mu}{d_p M_m a}\frac{dy}{dl} = r[1 - (1 - x_c)^{\sqrt{N_{Re}}}] \tag{26}$$

The left-hand side of Equation (24) is observed to be the *measured rate* at a point (or the measured rate in a differential reactor) and is equal to a fraction of the chemical reaction rate. The form of this result is shown in Figure 3. For the case of a first-order irreversible reaction at the catalyst surface, Equation (26) may be integrated to yield

$$\ln\frac{y_1}{y_2} = \frac{k\rho\, d_p M_m a}{\mu} \cdot \frac{[1 - (1 - x_c)^{\sqrt{N_{Re}}}]}{N_{Re}} \cdot L \tag{27}$$

The form of this result is shown schematically on Figure 4.

The application of these results to a particular situation, that is, the application of Equations (12), (25), and (27), requires knowledge of x_c. Of course, with the required data, it is possible to compute a value of x_c to characterize the reaction.

For a first-order irreversible reaction, δ_c may be estimated from the Nernst equation (*6*) thus:

$$\delta_c \approx \frac{D}{k} \tag{28}$$

From values of the molecular diffusivity and the chemical reaction rate constant k, δ_c may be estimated. Some values taken from the literature are shown in Table 1.

As in Equation (6), for $x_c \geq 1$, the incomplete beta function is unity, and Equation (12) reduces to the form for the reaction-controlled situation. It is apparent that except for very large operations, that is, large particle diameters, it is unlikely that diffusion will play a significant role in the reactions listed as *Set A* in Table 1. These reactions all show values of δ_c greater than 1 cm.; hence it appears that the particle diameter would have to be of this same order of magnitude before x_c becomes less than unity. For those cases listed as *Set B* one should expect some contribution from diffusion under certain conditions. Finally, for those reactions listed as *Set C*, it seems unlikely that rate-controlled situations will be observed in the laboratory since x_c is small. These conclusions are, in every case, in accord with the observations reported in the references cited.

There are a number of cases in the

TABLE 1

Reaction	Phase	Temp., °C.	k, cm./sec.	D, sq. cm./sec.	δ_c, cm.	Ref.
Set A						
1. Hydrogenation of ethylene	Gas	30	0.222	0.5	2.252	*1, 2*
2. Hydrogenation of ethylene	Gas	30	10^{-4}(approx.)	0.5	$5(10^3)$	*6*
3. Hydrogenation of propylene	Gas	30	0.053	0.5	9.433	*1, 2*
4. Hydrogenation of butene	Gas	30	0.104	0.5	4.807	*1, 2*
5. Decomposition of NH_3 on tungsten	Gas	631	.046	0.53	11.42	*4*
6. Dehydrogenation of ethyl benzene	Gas	30	0.0087	0.3	34	*7*
Set B						
7. Oxidation of carbon monoxide	Gas	299 319	28.4 58.3	0.675 0.717	0.023 0.012	*3* *3*
Set C						
8. Decomposition of HI on gold	Gas	705	$0.64(10^4)$	0.71	$1.1(10^{-4})$	*4*
9. Dissolution of zinc in acid	Liquid	27	$6.2(10^{-3})$	$0.5(10^{-5})$	$8(10^{-4})$	*5*

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literature which apparently do not afford a check of these conclusions. For example, Smith and Fuzek (*9*) report on the hydrogenation of furan and furan derivatives over solid catalysts suspended in acetic acid as a solvent. From their data, values of k for two cases can be computed to be 0.04-cm./sec. and 0.12-cm./sec. respectively. Since the value of the molecular diffusivity in liquids is quite small (about 10^{-5} sq. cm./sec.), one would expect these reactions to be diffusion controlled, as x_c is small. The authors, however, treat the data as though it were rate controlled. Similarly, the vapor-phase catalytic dehydrogenation of ethylbenzene is reported to be rate controlled (*10*). However, from the data presented one may calculate a value of the rate constant of 0.04-cm./sec., which with a value of diffusivity of approximately 0.2 sq. cm./sec., yields a value of δ_c equal to 5 cm. Thus, one might expect a significant contribution from diffusion. In such cases it is possible that the analysis of the data taken during the experimentation may be faulty or that the value of δ_c calculated by the method indicated does not serve as a definitive criterion for these cases.

Equation (25), then, is the principal result of this effort. It is in reality an empirical equation based on many *ad hoc* assumptions. Its value, if any, can become apparent only from attempts to use it with experimental data. This is essentially a *curve fitting* type of operation and has been done for several sets of data taken from published work. The "fit" obtained has been surprisingly good in those cases tested. Two specific examples will be presented.

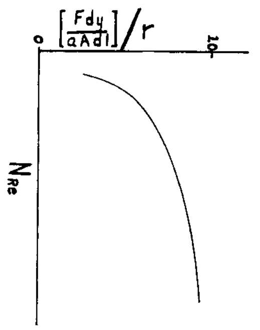
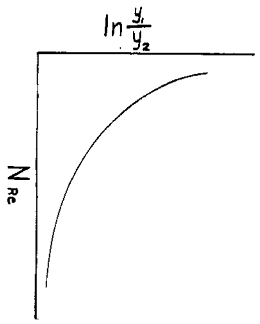


Fig. 3. Schematic representation of Equation (26).



↑ **Fig. 4. Schematic representation of Equation (27).**

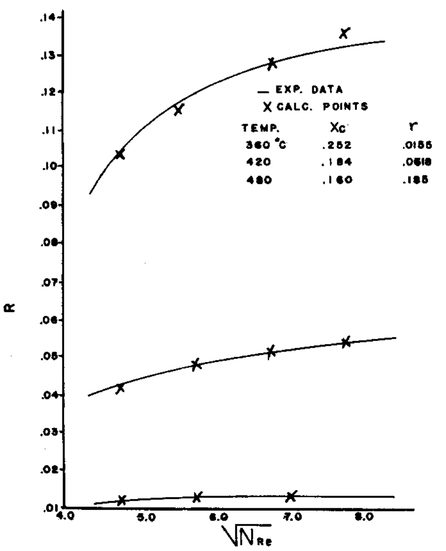


Fig. 5. Test of Equation (25) with data from reference *7*.

In the paper by Olson, Schuler, and Smith (*7*) on the catalytic oxidation of sulfur dioxide over a platinum catalyst, it is shown that the reaction is diffusion controlled over the range of variables studied. The analysis in this article is based on this assumption and proves generally reasonable and sound. Figure 9 of Smith's paper presents a set of rate-flow rate curves of the form shown herein as Figure 1. R is the rate reported for any given mass velocity G in lb./(hr.)(sq. ft.) and r is the maximum. Then, since a differential reactor was used, Smith's Equation (25) indicates that

$$R = r[1 - (1 - x_c)^{\sqrt{N_{Re}}}] \qquad (29)$$

where r and x_c must be obtained from the data presented. (The values of G tabulated in the paper were converted to Reynolds numbers by means of the physical data presented.) The result is shown herein as Figure 5. The solid lines represent the experimental data, whereas the points were computed from the equation and constants shown on the figure. The latter were obtained by a curve fitting process, and the fit is seen to be quite good.

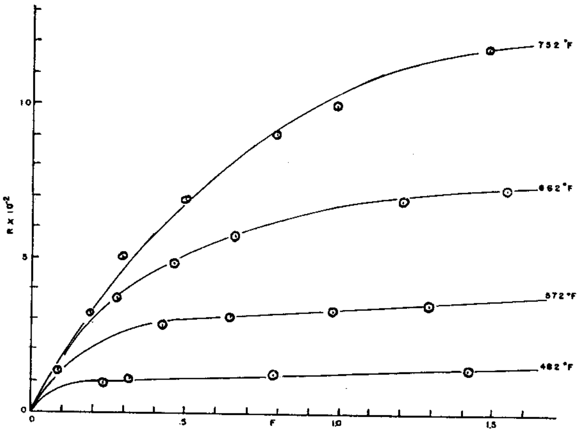
Since r should (physically) be equal to the surface or chemical reaction rate, it is possible to obtain a value of the energy of activation for the reaction. Values of r were plotted as the natural logarithm vs. the reciprocal of the absolute temperature and the slope determined to yield a value of 20,300 calories/mole for the energy of activation. This value is in reasonable agreement with previously reported values (*4* and *10*).

Finally, Hay, Coull, and Emmett (*2*) report on the catalytic isomerization of butene-1 and present data to indicate that the process is rate controlled. Specifically, Figure 7 of the reference paper presents a plot of space-time-yield vs. flow rate for several operating temperatures. The conversions reported by the authors are larger than those considered permissible in a differential reactor, and, hence, Equation (27) [the integrated form of (25)] was applied to these data. The result is presented herein as Figure 6. Again, the solid lines represent the experimental data, whereas the circumscribed points were computed from the equation and constants shown. The fit is again noted to be quite good. The values shown for x_c would again indicate that diffusion does play a significant role in the over-all mechanism, contrary to the statement of the authors. That this is true may be seen from an Arrhenius-type plot of the data (space-time-yield as the logarithm vs. $1/T$), the slopes of which yield values for an *over-all* energy of activation. Such a plot is shown in Figure 7. The effect of diffusion is evident in the variation of slopes on this figure. The variation of x_c with temperature is not unexpected in view of the temperature dependence of the terms comprising this constant.

From Equation (27) it is apparent that

$$C = \frac{k\rho\, d_p M_m a L}{\mu}$$

Hence, a value for the energy of activation of this reaction may be calculated from the temperature variation of C.



↑ **Fig. 6. Test of Equation (27) with data from reference *2*. R = space-time-yield, S.T.Y., reciprocal hr.; F = butene flow rate, lb.-moles/(sq. ft.)(hr.); solid lines = experimental data from reference *2*; points computed by use of Equation (27), viz:**

$$\ln y_1/y_2 = C\,\frac{[1 - (1 - X_c)^{\sqrt{N_{Re}}}]}{N_{Re}}$$

with the following values of the constants

T°, F.	X_c	C
482	0.397	1.025
572	0.678	1.980
662	0.450	4.550
752	0.390	8.000

This was done to yield a value of 12,500 cal./mole. At the highest flow rate and lowest temperatures shown on Figure 7 of this paper, a condition which is most likely to yield a reaction-controlled situation, the slope of the line yields a value of E of 12,360 cal./mole.

Finally, the authors present a plot of H_r vs. $1/T$ and indicate that the resulting straight line constitutes proof that the process is rate controlled. It may be seen, however, that the three data points at the highest temperatures may easily be interpreted as a portion of the curve yielding an increasing downward slope. This would correspond to an increasing influence of diffusion, in accordance with the definitions of H_r. The slope of the line through the low-temperature data yields a value for the energy of activation of the reaction studied of approximately 11,000 cal./mole, again in good agreement with the values calculated from flow-rate consideration and from the constant C.

SUMMARY AND CONCLUSION

A method has been developed for predicting the performance of a fixed-bed catalytic reactor when the surface (chemical) reaction rate is known or for predicting the surface rate when something of performance is known, even though the available data cover only the diffusion-controlled range of operation. The method is empirical and, like other such techniques, involves two empirical constants. Thus, the equations presented offer no advantage in the sense of degree of freedom. However, the method presented in this paper focuses attention on a property of packed beds which has been virtually neglected to date, namely the inescapable conclusions that the areas in a bed are *not* uniformly available to the fluid and that the film thicknesses throughout the bed vary according to some distribution law.

The basic idea of this paper is not restricted to the problem of a fixed-bed catalytic reactor but applies equally well to any problem involving contact of a fluid or fluid constituent with the surface of a solid in a packed bed. Such problems as adsorbers, absorbers, etc., should be amenable to treatment in much the same manner.

In a consideration of the applicability of this technique to reactors, it is highly possible that the major advantage of the method may become more apparent in reactions of higher orders than unity. The use of averaged and distributed film thicknesses yields essentially the same numerical over-all conversion rates for first-order reactions. A more detailed study of the present proposal for the case of higher ordered reactions is indicated.

The present method, therefore, is of interest chiefly because it initiates a way of looking at these problems, a method which demands consideration of the point-to-point variation of film thicknesses throughout the bed. While the method offers no dramatic advantage over more standard approaches for the case of a purely diffusion-controlled situation, it does permit computation of the surface-reaction-rate constants for the chemical step from data taken in the diffusion range. This is not possible by more "classical" approaches. In addition, significant advantages for the case of higher order reactions appear likely.

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NOTATION

A = cross sectional area of bed, sq. cm.
a = catalytic surface area per unit volume, sq. cm./cc.
a' = constant—defined by Equation (19), dimensionless
a_c = catalytic surface area per unit volume, over which $1/\delta_c < 1/\delta < \infty$, sq. cm./cc.
a_d = catalytic surface area per unit volume, over which $1/\delta_{max} < 1/\delta < 1/\delta_c$, sq. cm./cc.
B_x = incomplete beta function defined by Equation (5)
b = constant—defined by Equation (19), dimensionless
C_i = surface concentration of reactant, moles/cc.
C_0 = free stream concentration of reactant, moles/cc.
D = molecular diffusivity, sq. cm./sec.
dl = element of bed length
d_p = particle diameter, cm.
E = energy of activation, cal./mole
F = flow rate, moles/sec.
G = mass rate of flow; mass/(sq. cm.)(sec.)
j_d = j factor
k = reaction rate constant, cm./sec.
kg = mass transfer coefficient, moles/(sq. cm.)(sec.)
L = bed length cm.
Mm = mean molecular weight, g./mole
N_{Re} = Reynolds number based on empty cross sectional area of bed, dimensionless
N_{Sc} = Schmidt number, dimensionless
R = gas constant, cal./mole°
r = surface (chemical) reaction rate, moles/(sq. cm.)(sec.)
r_d = rate of diffusion of reactant to the surface; moles diffusing per unit time per unit of surface area
T = temperature, °K.
V = volume, cc.
x = dimensionless boundary layer thickness
y = mole fraction of reactant

Greek Letters

α = constant, defined by Equation (3), dimensionless
β = constant, defined by Equation (3), dimensionless
δ = boundary-layer thickness, cm.
δ_c = critical boundary-layer thickness cm.
δ_{max} = maximum boundary-layer thickness, cm.
ρ = average molal density, moles/cc.

Subscripts

0 = free stream condition
1 = inlet condition
2 = outlet condition

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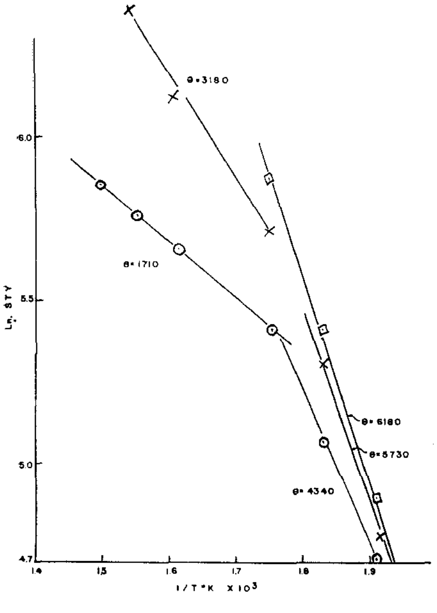

Fig. 7. Arrhenius plot of over-all data from reference *2*. S.T.Y. = space-time-yield, reciprocal hr., *T* = temp., °K., ⊙ = data points for *F* = 0.2 lb.-moles butene/(sq. ft.)(hr.), *x* = data points for *F* = 0.5 lb.-moles butene/(sq. ft.)(hr.), ⊡ = data points for *F* = 1.6 lb.-moles butene/(sq. ft.)(hr.), ⊖ = *E*/*R* = slope.